Effect of organosulphur, organonitrogen and organooxygen compounds on the hydrodechlorination of tetrachloroethylene over Pd/Al$_2$O$_3$

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Abstract

The performance of a 0.5 wt.% Pd on alumina catalyst used for the hydrodechlorination of tetrachloroethylene, in presence of model organosulphur (thiophene and butanethiol) organonitrogen (quinoline and *n*-butylamine) and organooxygen (tetrahydrofurane, isobutanol) compounds, was studied in this work. Experiments were carried out in a continuous fixed bed reactor (space time of 1.8 min g/mmol of TTCE) at a pressure of 0.5 MPa and a temperature range of 200–300 °C. Concentrations of heteroatomic molecules in the range 0.5–5% were used in this study.

Organosulphur compounds produce strong inhibition on the TTCE hydrodechlorination, decreasing the conversion and increasing the selectivity for partially dechlorinated compounds (trichloroethylene). However, this effect is shown to be highly reversible, the catalyst almost recovering its initial activity when the sulphur source is removed from the feed. Organonitrogen compounds cause a fast and fatal deactivation of the catalysts, being this effect completely irreversible. Different regeneration procedures were tested, being the treatment with hydrogen at 400 °C the only way to partially recover catalytic activity. Finally, organooxygen compounds hardly affect catalyst performance.

1. Introduction

The management of organic wastes from dry-cleaning facilities and textile industries is a major environmental problem. In the most of the modern installations, tetrachloroethylene-based solvents are used for textile cleaning. In order to enhance the properties of the solvent (detergency, viscosity, etc.), variable amounts of other organic compounds (such as hydrocarbons, amines, esters) are added to the chlorinated solvent TTCE [1]. In the modern installations, the used solvent is distilled, purified TTCE being reused in the process. However, the bottoms of this process have high concentration of TTCE (up to 40%), as well as most of the additives of the fresh solvent and greases coming from the cleaning process. This waste (viscous liquid or solid, depending on operation conditions), which is water-insoluble and very soluble in organic solvents, is considered as a hazardous waste because of its high content of TTCE. This chlorinated compound is considered as a dangerous pollutant because of their both short-term (skin irritant, causes lung and central nervous system diseases) and long-term (liver and kidney diseases, potential carcinogenic effects) effect on human health [2].

Catalytic hydrodechlorination (HDC) could be a safe alternative treatment for these wastes, as recently stated in the European Reference Documents (BREF) on Best Available Techniques for Waste Treatment [3]. Catalytic HDC consists of reacting the organochlorinated compounds with hydrogen in the presence of a catalyst, yielding hydrogen chloride, that can be easily removed, and, if HDC is complete, hydrocarbons, which can be burned or even recovered as valuable chemicals. HDC presents relevant environmental advantages, such as the no formation of harmful by-products as Cl$_2$, fragments of parent chlorocarbons, COCl$_2$ or other oxidation by-products, very common in oxidative treatments. This technique was also proposed for the treatment of gaseous [4] and aqueous streams [5].

In order to operate at mild conditions, HDC of most chlorinated compounds requires the presence of a catalyst. The

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most extensively studied catalysts for HDC reaction in organic medium are hydrotreatment catalysts (typically promoted metal sulphides).

They operate at relatively severe conditions (typically 10 MPa, $T > 350\,^\circ$C), and are not stable in the presence of HCl [6]. Precious metals (Pd, Pt, Rh) are more expensive, but are more active and work at milder conditions (0.1–0.5 MPa, 250 °C). Research carried out by our group on HDC of chloro-aliphatic compounds over different precious metals and supports showed that Pd on alumina presents the best combination of activity and stability [7]. The influence of process parameters, such as temperature, pressure, hydrogen/organic compound ratio and nature of solvent, on the performance of this catalyst was also studied [8,9]. Results indicate that high hydrogen/organochlorinated compound ratio favours conversion and catalyst stability, the presence or nature of the organic solvent (it must taken into account that the treatment of these wastes involves the dissolution in organic solvents) has no relevant effect, while temperature has a two-fold effect: higher temperature leads to higher initial conversion, but faster catalyst deactivation. Generally, it is observed that the main deactivation cause is the formation of coke deposits, promoted by the surface acidity increase caused by the HCl released in the reaction [8,9]. The presence of strong inhibition effects when different chlorinated are processed together was also observed [10,11].

However, when catalytic hydrogenation is applied to real wastes (as in the case of the wastes from dry-cleaning facilities), other organic compounds could be present. Many of these compounds are hydrocarbons, which are reported to no significantly affect the performance of this process [8]. But some of these organics can contain other heteroatoms, such as sulphur, nitrogen or oxygen. The presence of these elements, as well as their hydrogenation products: H_2S, H_2O and NH_3, can severely affect catalyst performance. Because of their chemical similarities, there are several works studying parallel hydro-dechlorination, hydrodenitrogenation (HDN) and hydrodesulphurization (HDS), but most of these works deal with hydrotreatment catalysts [6,12,13]. So, it is well established that the presence of organosulphur compounds does not affect catalyst performance, whereas the H_2S released in the reaction even enhances the hydrodechlorination reaction [6]. The hydroprocessing of molecules with both chlorine and sulphur (typical in some warfare agents) was successfully studied by Jang and Spivey [13], not observing any kind of deactivation.

The studies are much scarcer in the case of noble metal catalysts. Typically, these catalysts were considered not suitable in presence of organosulphur compounds. However, recent works are focused on HDS over Pd catalysts, as they are considered as appropriate catalysts for ultra-deep HDS [14]. In these cases, organonitrogen compounds (specially aromatic ones) are observed to severely inhibit HDS reaction [15]. In the same way, Xia et al. [16] observe that pyridine cause severe inhibition in the hydrodechlorination of oxychlorinated compounds over Pd catalysts, whereas other organooxygen compounds (such THF) does not markedly affect the catalyst performance. In a previous work, we observed that TPN

inhibits the TTCE hydrodechlorination, being this effect modelled considering a Langmuir-Hinselwood mechanism with competitive adsorption of TPN and TTCE [17]. It was also observed that this inhibition effect decrease both TTCE conversion and selectivity towards fully dechlorinated products.

In spite of the practical importance of the effects of these sulphur-, nitrogen- and oxygen-containing organic compounds on catalytic hydrodechlorination, there are not, to the best of our knowledge, systematic studies on the effect of this compounds in the deactivation of the palladium catalysts used for TTCE hydrodechlorination. So, in this work, the effect of the main heteroatoms on the HDC of TTCE is investigated. For this purpose, the performance of a Pd/Al_2O_3 catalysts will be studied in presence of different organosulphur (thiophene and butanethiol, BTT), organonitrogen (quinoline, QNL and butylamine, BTA) and organooxygen (tetrahydrofurane, THF and isobutanol, ISB) compounds.

2. Experimental

2.1. Materials

The chemicals used in this work (TTCE, TPN, BTT, QNL, BTA, THF, ISB, trichloroethylene (TCE), toluene, methylcyclohexane and decahydronaphtalene) were supplied by Panreac, Fluka, Janssen and Merck, with a minimum purity of 99%. Hydrogen C-50 was supplied by Air Products with a minimum purity of 99.999%. The catalyst tested was Engelhard Escat 16, a commercial γ-alumina-supported Pd catalyst, with composition and textural characteristics given in Table 1. The catalyst is available as pellets, which were crushed and sieved to a particle size between 0.250 and 0.355 mm. Inert α-alumina (Janssen) was used to dilute the catalyst introduced in the reactor.

2.2. Reaction studies: equipment and experimental procedure

Reactions were carried out in a fixed-bed reactor consisting of a 9 mm i.d., 450 mm long stainless steel cylinder, placed inside a PID-controlled tubular electric furnace and equipped with five thermocouples at different reactor heights for temperature monitoring. The catalyst (typically 0.5 g) mixed with α-alumina was placed in the mid-section of the reactor. The bottom and top sections were packed with 1 mm glass spheres, the upper part being used as pre-heating zone. Before starting the reaction, the catalyst was activated in situ by passing through the reactor, heated at 350 °C, 0.90 L/min (measured at standard conditions) of hydrogen at 0.5 MPa for

Table 1
Composition and textural properties of catalyst Engelhard Escat 16

Composition (wt.%)	0.5% Pd/Al_2O_3
BET specific surface (m²/g)	92
BJH desorption pore volume (cm³/g)	0.46
Average pore diameter (nm)	18

6 h. The liquid and gas feeds flowed co-currently downwards through the reactor. The liquid feed (toluene, 10% (w/w) of TTCE and S, N or O-containing compound) was pumped by a Kontron T-414 liquid chromatography pump, working at space time of 1.8 g min/mmol of TTCE. At reaction conditions, the liquid feeds were completely vaporized. The reactor gas feed was pure hydrogen, with flow rate controlled by a Brooks 5850 TR/X mass-flow regulator.

The reaction products were collected in a stainless steel Teflon-lined cylindrical receiver. The top of the receiver was connected to a Tescom 26-1723-24 back-pressure regulator, which maintained the operating pressure (0.5 MPa, selected to ensure that most reaction products remained in liquid phase). Liquid samples were collected by emptying the receiver at selected time intervals. All the elements of the reactor set up were constructed in Hastelloy-C, resistant to the corrosion caused by HCl. The set up was fitted with safety features, such as temperature and pressure controls, and a rupture disk.

2.3. Analysis and catalyst characterization

Reaction products were analysed by gas chromatography in a Shimadzu GC-17A apparatus equipped with a FID detector and a HP-1 30 m capillary column, using decahydronaphtalene as internal standard. The oven was maintained at 30 °C for an initial period of 15 min, and then heated to 180 °C at 6 °C/min. Peak assignment was performed by GC-mass spectra and responses were determined using standard calibration mixtures. In all the experiments reported in this work, tetrachlorethylene hydrodechlorination only yields trichloroethylene and ethane. Fractional conversions and selectivities were calculated from the concentration of reactants and products in the inlet an outlet streams. Chlorine mass-balance was periodically checked by measuring the HCl concentration in the outlet gaseous stream (previous solution in alkaline water and chloride tritation). The formation of NH_3 and H_2S was followed with an electrochemical detector (Dräger MiniWarm), whereas the formation of permanent organic gases (such as ethane or propane) was determined by GC, using a Carbowax column and a TCD detector.

When the reaction was stopped, the catalyst was cooled by flowing nitrogen through the system, separated from the inert alumina by sieving and collected for subsequent characterization. Catalysts samples were characterized by several techniques. Nitrogen adsorption measurements were performed in a Micromeritics ASAP 2000 apparatus. Values of surface area and pores volume were calculated using the methods of Brunauer-Emmett-Teller and Barrett-Joyner-Halenda, respectively. Thermogravimetric studies were carried out in order to evaluate the carbonaceous deposits on the used catalysts in a Mettler TA4000-TG50 thermobalance, in a synthetic air oxidant atmosphere. Temperature-programmed oxidation (TPO) and reduction (TPR) studies were performed in a Micromeritics TPD-2900 apparatus, equipped with TCD detector, and connected to a Gaslab mass spectra analyser. Studies were carried out by flowing 29 mL/min of 2 vol.% O_2/ balance He (TPO) or 10 vol.% H_2/balance Ar (TPR) on the

catalyst samples heated at 10 °C/min. Morphological studies were made by scanning electron microscopy (SEM) in a JSM-6100 JEOL microscope, equipped with a EDX Link eXL-1000 microanalysis apparatus, and by transmission electron microscopy (TEM) in a JEOL JEM2000EXII microscope operating between 160 and 180 kV.

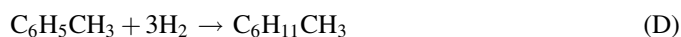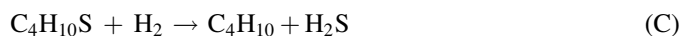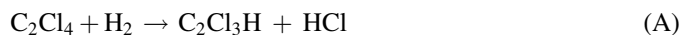## 3. Results and discussion

3.1. Effect of organosulphur compounds

3.1.1. Reaction studies

The performance of the catalysts in presence of the studied heteroatomic compounds was studied at a space time of 1.8 min g/mmol of TTCE, 0.5 MPa total pressure and a temperature range of 200–300 °C. At these reaction conditions, it was observed in previous works that the catalyst performs without significant deactivation for more than 100 h for the hydrodechlorination of TTCE in absence of the studied compounds [9]. In the same work, it was observed that even the effect of externally added HCl on catalyst stability is not significant up to concentration of HCl of 5%.

The first set of experiments was carried out feeding the reactor with a liquid feed consisting of 0.5 mL/min of 10 wt.% TTCE dissolved in toluene, adding 0.5 wt.% of organosulphur (TPN or BTT) at selected time intervals. The reactor gas feed was 2.3 L/min (STP) pure hydrogen that corresponds to 50 times the stoichiometric amount (calculated supposing that all TTCE reacts to ethane, all BTT and TPN react to butane and 5% of toluene reacts to methylcyclohexane). Experiments were carried out at 5 bar and 250 °C. The liquid feed contained only TTCE in toluene during the first 50 h; then, sulphur compound was continuously added during the next 28 h, or up to total deactivation. Finally, the feed was changed again to TTCE in toluene free of organosulphur compound.

In all the cases, the reaction products detected were TCE, ethane, butane and methylcyclohexane (by GC) and hydrogen chloride and hydrogen sulphide. The reactions taking place are the following:

$$C_2Cl_4 + H_2 \rightarrow C_2Cl_3H + HCl \qquad (A)$$

$$C_2Cl_3H + 4H_2 \rightarrow C_2H_6 + 3HCl \qquad (B)$$

$$C_4H_{10}S + H_2 \rightarrow C_4H_{10} + H_2S \qquad (C)$$

$$C_6H_5CH_3 + 3H_2 \rightarrow C_6H_{11}CH_3 \qquad (D)$$

In previous works, we have observed that the reactivity of TTCE and TCE is very similar, whereas dichloroethylenes and vinyl-chloride are very reactive [10]. This is justified in the literature considering a reaction mechanism consisting of successive hydrogenation–dehydrochlorination steps. The first step is normally the controlling one, being more favoured as the number of chlorine atoms joined to the double bond decreases [18]. This is the cause why other chlorinated compounds are not detected in quantifiable amounts.

Fig. 1 shows the evolution of TTCE conversion and TCE selectivity with time on stream, when the effect of BTT on
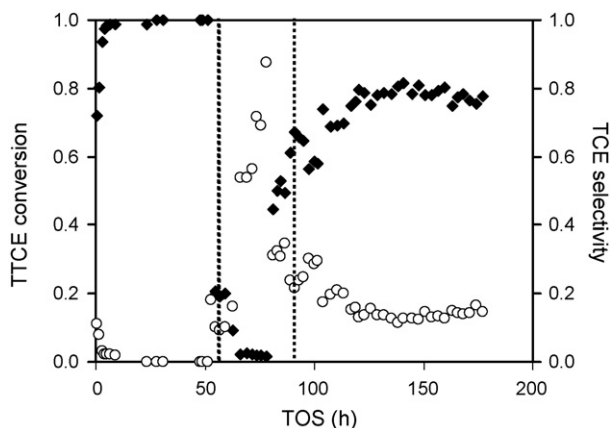
Fig. 1. Evolution of TTCE conversion (◆) and TCE selectivity (○) with time on stream (TOS) for the hydrodechlorination of 10 wt.% TTCE dissolved in toluene at 5 bar and 250 °C. BTT (0.5%, w/w) was added during the period 50–78 h.

Fig. 3. Evolution of TTCE conversion (◆) and TCE selectivity (○) with time on stream (TOS) for the hydrodechlorination of 10 wt.% TTCE dissolved in toluene at 5 bar and 200 °C. TPN (0.5%, w/w) was added during the period 50–115 h.

catalyst performance was studied. TTCE conversion decreases sharply to nearly 0 when BTT is added to the reaction feed. When BTT is removed from the feed, TTCE conversion increases gradually, although the recovery in TTCE conversion is not complete. The evolution of TCE selectivity is the opposite: TCE selectivity increases in presence of BTT and decreases again in absence of BTT. After 170 h on stream, the catalyst is still active for TTCE hydrodechlorination, although TTCE conversion is significantly lower (about 20%) than before the BTT addition, and TCE is formed in appreciable amounts.

The effect of the TPN on TTCE hydrodechlorination is shown in Fig. 2. In general terms, the behaviour is similar to the one observed for the same reaction in presence of BTT. TTCE conversion drop in presence of TPN was less pronounced, and the recovery of TTCE conversion and TCE selectivity when TPN was removed from the reaction feed was almost complete. This result (showing that the effect of TPN is essentially inhibition rather than deactivation) is in a good agreement with
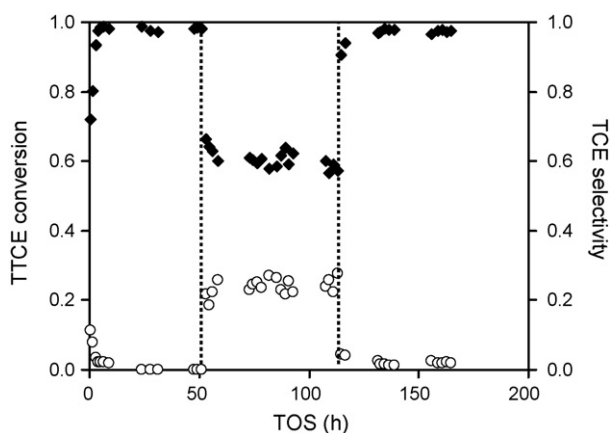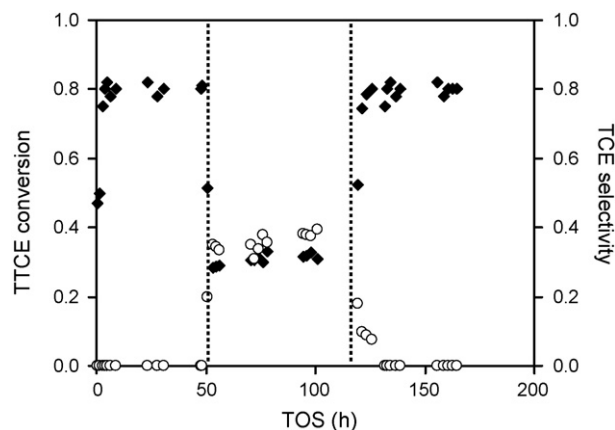
literature findings that model the kinetics of the hydrogenation of TTCE-TPN mixtures using Langmuir-Hinshelwood kinetics considering competitive adsorption of both organic compounds [17].

In order to evaluate the effect of the temperature on the poisoning effect, the experiment was repeated at 200 °C. Results, depicted in Fig. 3, show that the decrease in the TTCE conversion and the increase in the TCE selectivity are more marked as the temperature decreases. This fact suggests that the adsorption of the TPN plays a key role in the catalyst poisoning. It should be noted that adsorption equilibriums are exothermic and hence favoured as temperature decreases.

Fig. 4 shows the evolution of BTT and TPN conversions with time on stream during the period in which they are fed to the reactor. It can be observed that initial conversion is notably higher for BTT, and that both conversions decrease gradually with time. This result is in a good agreement with the reported trends for hydrodesulphurization, being traditionally accepted that terminal sulphur atoms are easier to remove [19]. The

Fig. 2. Evolution of TTCE conversion (◆) and TCE selectivity (○) with time on stream (TOS) for the hydrodechlorination of 10 wt.% TTCE dissolved in toluene at 5 bar and 250 °C. TPN (0.5%, w/w) was added during the period 50–110 h.
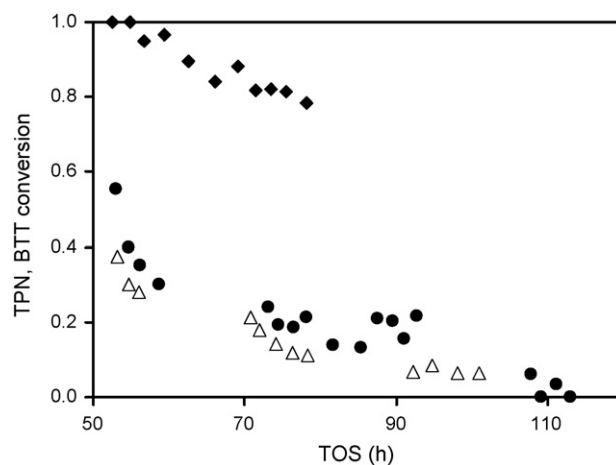

Fig. 4. Evolution of BTT (◆) and TPN conversions with time on stream (TOS) during the period at which the sulphur-containing compound was added to the reaction feed. TPN conversion data is reported at 200 °C (△) and 250 °C (●).

Table 2
Summary of the main parameters of the deactivated catalysts studied in this work: fresh catalyst (A), catalyst deactivated at 200 °C in absence of heteroatom compound (B), catalyst deactivated at 200 °C in presence of TPN (C), catalyst deactivated at 250 °C in presence of TPN (D) and catalyst deactivated at 250 °C in presence of QNL (E)

	Catalyst				
	A	B	C	D	E
Specific surface area (BET)	92	86	85	85	60
Average crystallite diameter (TEM)	8.2	12.3	11.9	12.2	[a]
Weight loss (200–800 °C, TG)	0	4.1	2.1	3.1	8.1

[a] Not measurable.

higher conversion attained by BTT, resulting in higher hydrogen sulphide concentration in the reaction mixture, can explain the stronger inhibition observed for BTT. In the same way, results suggest that H_2S plays a key role in the irreversible deactivation.

3.1.2. Catalyst characterization

In order to elucidate the effect of the presence of organosulphur compounds on the catalyst, different catalyst samples were characterized. For this purpose, three different deactivation experiments were carried out for 23 h reaction time: working with the conventional TTCE-toluene feed (200 °C) and adding 0.5% of TPN (at 200 and 250 °C). Measured BET surface areas (summarised in Table 2) were 92 m^2/g for the fresh catalyst, 86 m^2/g for the catalyst used for TTCE hydrodechlorination with no TPN and 85 m^2/g for the catalyst in presence of TPN (at both temperatures). Hence, the presence of TPN has no relevant effect on the BET surface area. SEM observations at 10,000 magnifications showed no significant morphological changes, between all the aged catalysts.

Pd crystallite size distributions were determined by TEM, measuring the size of more than 80 crystallites for samples of catalyst, fresh, reacted with TTCE at 200 °C for 23 h, and reacted at the same conditions in presence of TPN. The resulting average crystallite size, calculated according to the procedure outlined in reference [9] is 8.2 nm for the fresh catalyst, 12.3 nm for the catalyst reacted in absence of TPN, and 11.9 and 12.2 nm for the catalyst reacted with TPN at 200 and 250 °C, respectively (Table 2). These results indicate that the presence of sulphur compounds does not markedly modify the dispersion of the active phase. So, although in the literature is reported that sulphur enhances metal particle sintering at relatively low temperatures [20], this behaviour has not been observed in this work.

The amount of carbonaceous deposits on the catalysts was measured by thermogravimetry, according to the procedure outlined in the literatures [21,22]. The values of weight loss (between 200 and 800 °C) and main combustion peak are 4.1% and 404 °C for the catalyst reacted in absence of TPN, 2.1% and 390 °C for the catalyst reacted in presence of TPN at 200 °C and 3.1% and 405 °C for the catalyst reacted in presence of TPN at 250 °C. It should be noted that there are not correlation between the BET surface area and the coke content. This fact

suggests that coke is deposited in thin layer over the support, not affecting the pore volume. This behaviour is commonly found both a mesoporous support is used and coking is not the main deactivation cause [8].

These three samples were also analysed by TPO-MS, in order to determine the nature of the weight losses. TPO-MS profiles are shown in Fig. 5A (CO_2 release signal) and Fig. 5B (SO_2 release signal). In the case of HCl release, it follows a very similar trend for all the studied catalysts, being released at temperatures higher than 600 °C.

Results, which are in good agreement with the TG parameters, shows that the amount of coke of the aged catalysts is markedly lower in the case of TPN-treated catalysts. It is assumed that the combustion temperature of carbonaceous deposits depends on its chemical structure and the strength of the interaction between the deposit and the catalyst [7,22]. From this point of view, there are not relevant differences in this temperature, revealing that the sulphur compound does not modify the coke properties. However, important differences are observed in the amount of coke of the material. In general, it is observed that TPN-treated catalysts bear lower amounts of coke, decreasing this amount with the reaction temperature.
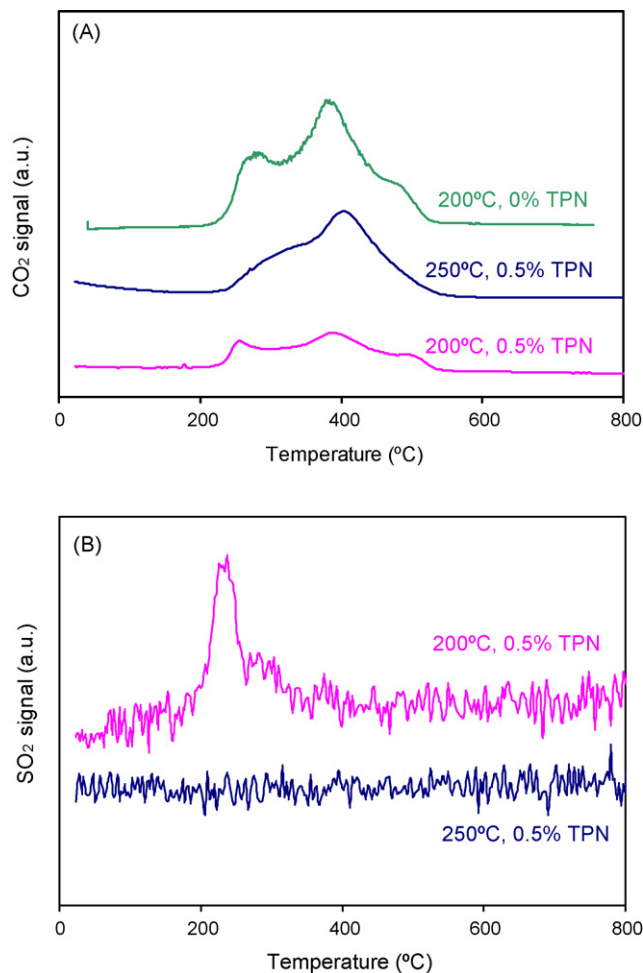

Fig. 5. Evolution of the CO_2 (A) and SO_2 (B) releases with temperature during the TPO analysis of the catalysts aged in absence of TPN (200 °C) and in presence of a 0.5% of TPN (at 200 and 250 °C).

The last point is a good agreement with the behaviour observed during the HDC of tetrachloroethylene [8,9], whereas the former one suggests that the presence of sulphur compounds also inhibit the formation of coke. This fact is explained considering that coke formation is catalysed by both metal particles and alumina acid sites [9,23], TPN being adsorbed on both types of sites.

Concerning SO_2 release, it is observed only in the case of the catalyst poisoned at the lowest temperature, being not associated to CO_2 emission. This result suggests that this release corresponds to the decomposition of labile metal sulphides. These sulphides are considered in the literature as an important deactivation cause for hydrogenation reactions [24,25]. The formation of these sulphides involves the adsorption of the H_2S formed during the TPN hydrogenation, and the reaction of the H_2S with the Pd. The first one is an exothermic process (favoured as temperature decrease), whereas the second is endothermic (favoured at increasing temperatures). Our results suggest that the first one is the controlling step.

From the results obtained, it could be concluded that the adsorption of organosulphur compounds leads to strong inhibition effects (reversible) whereas the formation of Pd sulphides could lead to irreversible deactivation.

3.2. Effect of organonitrogen compounds

3.2.1. Reaction studies

The effect of the presence of organonitrogen compounds on the catalytic hydrodechlorination of TCE has been studied by adding 0.5 wt.% of quinoline or butylamine (model for aromatic and aliphatic compounds, respectively) to the reaction feed (10 wt.% TCE in toluene). The experimental procedure and conditions were similar to those reported in the previous section. The reaction products detected were ethane, hydrogen chloride, TCE and traces of 1,2,-dichloroethene (from TTCE) and methylcyclohexane from toluene. Concerning to the nitrogenated compounds, BTA hydrogenation products were butane and ammonia, whereas the hydrodenitrogenation of QNA yields ammonia and a complex mixture of products including propylbenzene, *o*-propylaniline, tetrahydroquinoleine, 1,2,3,4,-tetrahydroquinoline, 1-ethyl-2,3-dimethylbenzene and 2-amine-5-chloropyridine. In the case of aliphatic amines, it is well accepted that the reaction follows a direct C–N bond hydrogenation, yielding the main reaction products [26]. However, in the case of aromatic organonitrogen compounds reaction mechanisms are more complex, since the direct breakage of C–N bond is not possible in these structures. So, different mechanisms are proposed in the literature, including dearomatization–elimination and substitution steps [26,27]. It is also reported that the presence of other inorganic gases, such as H_2S can participate in the reaction pathways through amine substitutions [28]. Although, a detailed study of these reaction pathways is out of the scope of this work, the presence of HCl could largely modify the reaction pathways.

The evolution with time on stream of TTCE conversion, TCE selectivity and QNL or BTA conversion are represented in
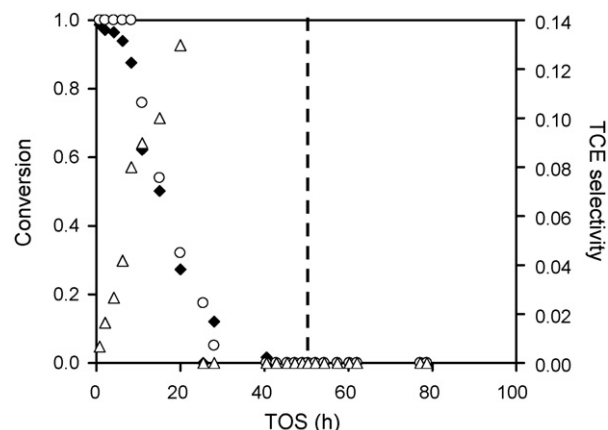

Fig. 6. Evolution of TTCE conversion (◆), TCE selectivity (△) and QNL conversion (○) with time on stream (TOS) for the hydrodechlorination of 10 wt.% TTCE dissolved in toluene at 5 bar and 250 °C. QNL (0.5%) was added during the period 0–50 h.
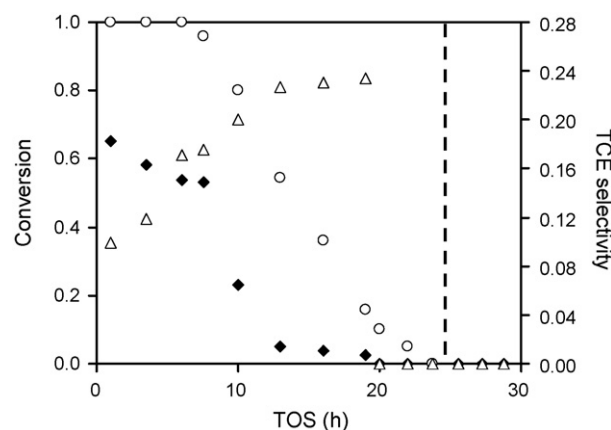

Fig. 7. Evolution of TTCE conversion (◆), TCE selectivity (△) and BTA conversion (○) with time on stream (TOS) for the hydrodechlorination of 10 wt.% TTCE dissolved in toluene at 5 bar and 250 °C. BTA was added during the period 0–25 h.

Figs. 6 and 7, respectively. The presence of either QNL or BTA leads to a sharp decrease in TTCE conversion and an increase in TCE selectivity. Thus, the catalyst is completely deactivated after 10 h on stream in presence of organonitrogen compound. Conversions of nitrogen-containing compounds, initially very high, also drop. When QNL or BTA are removed from the reaction feed, conversions remain near zero, without appreciable deactivation. In both experiments, a gradual increase in the pressure drop through the reactor was observed.

3.2.2. Catalyst characterization

The catalyst recovered after the reactions showed the presence of solid deposits, visible to the naked eye, which are supposed to cause the aforementioned gradual increase in pressure drop. The deposits corresponding to the experiment with QNL were dissolved in 250 mL water, and the resulting solution analysed by the Nessler method, resulting in a concentration of NH_4^+ in the solution of 210 ppm. The solid deposits were also evident by SEM, in the form of approximately 300 nm long particles, and
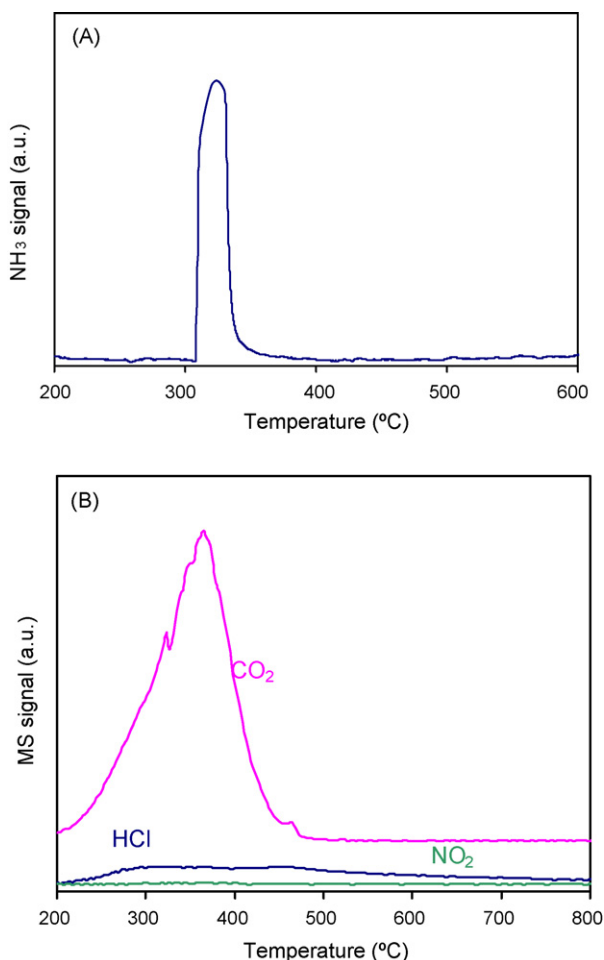
Fig. 8. Ammonia release profile during the TPR (A) and CO_2, HCl and NO_2 release profiles during the TPO (B) of the catalyst deactivated in presence of QNL (250 °C).

produced an important decrease in surface area and pore volume (BET surface area of 60 m^2/g).

Deactivated catalysts were analysed by TPR (Fig. 8A). Recorded MS patterns show a sharp peak of ammonia release, being the maximum of this peak at 327 °C. This peak suggests the presence of strongly chemisorbed nitrogen compounds, which would be hydrogenated at these temperatures. On the other hand, TPO analyses of the deactivated catalysts show that the combustion of the carbonaceous deposits takes place at lower temperatures (main combustion peak at 360 °C for the catalyst poisoned with quinoleine, Fig. 8B), whereas very small amounts of NO_2 are released at the same time, suggesting the presence of small amounts of nitrogen in these deposits.

These results suggest the presence of two concomitant deactivation causes: inhibition caused by the strong adsorption of nitrogen compounds and fouling caused by the formation of ammonium or alkylammonium chlorides. The first effect is widely reported in the literature, organonitrogen or even ammonia are considered as strong inhibitors in different hydrogenation reactions because of its marked Lewis base character [12,29–31]. However, to the best of our knowledge, this fouling behaviour has not been reported yet.

3.2.3. Catalyst regeneration

Three different procedures were tested in order to regenerate the catalyst deactivated in presence of QNL. In two of these cases, the reactor was emptied, the solid content recovered, dried overnight at 80 °C, and the catalyst particles separated from the inert material by sieving.

The first regeneration method, aimed to separate the ionic solids deposited on the catalyst surface, consists of two successive washings (during 6 h)–filtering–drying sequences using acetone (in order to remove organic materials) and boiling water (in order to remove ionic solids). After this treatment, the catalyst was filtered, dried overnight at 100 °C and introduced again in the reactor. The catalyst treated in this way showed no appreciable recovery of the catalytic activity.

The second method was devoted to solve the solid organic deposits from the catalyst. It consisted of washing in a Soxhlet apparatus with toluene and cyclohexene. This method has been shown to be effective for removing carbonaceous deposits from hydrogenation catalysts used in reactions with high coke deposition rates, such as polyaromatics hydrotreating [32]. The catalyst was then filtered, dried overnight at 110 °C, and introduced in the reactor. This method did not lead to a significant recovery of the catalytic activity.

TPR results previously commented, which showed a strong ammonia peak at 327 °C, suggested another possible method for catalyst regeneration through the hydrogenation of the nitrogen compounds. The method consisted of interrupting periodically the reaction feed during the reaction, and treating the catalyst in situ with hydrogen above 327 °C (in this case at 400 °C for 15 min, every 8 h). Results obtained are shown in Fig. 9. This method is partially effective in regenerating the catalyst, although TTCE conversion decreased continuously, TCE selectivity increased, and pressure drop through the reactor increased gradually, so that the reaction had to be stopped after approximately 30 h. The partial character of this regeneration can be explained considering that the hydrogenation step lead to only a partial gasification of the deposits, rather
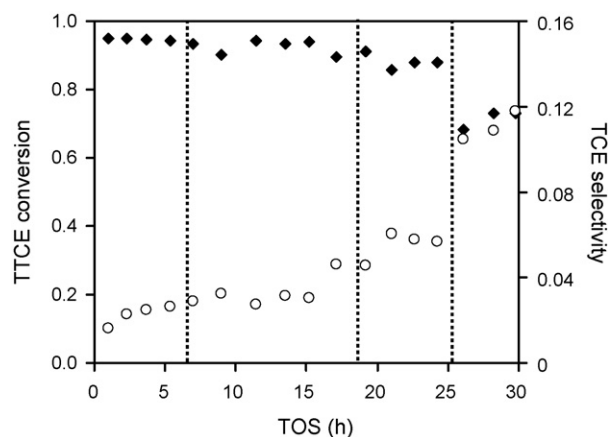

Fig. 9. Evolution of TTCE conversion (◆) and TCE selectivity (○) with time on stream (TOS) for the hydrodechlorination of 10 wt.% TTCE dissolved in toluene in presence of 0.5% of QNL at 5 bar and 250 °C. Catalyst treated with hydrogen at times marked with dotted lines.

that the sintering of active phase during the thermal treatment (catalysts was only 45 min at 400 °C).

From a practical point of view, the usefulness of this method regeneration method is rather limited, because, although the bed blocking by the deposition of solids could be diminished using bigger catalyst particles, or other reactor configurations, the reactivation method is not able to prevent the pronounced drop in the yield of total hydrodechlorination products.

3.3. Effect of organooxygen compounds

The effect of the presence of organooxygen compounds on the catalytic hydrodechlorination of TTCE has been studied by adding tetrahydrofurane (model for aromatic compounds) and isobutanol (model for aliphatic compounds) to the reaction feed. The experimental procedure and conditions were similar to previous experiments, working at a temperature of 250 °C. The main reaction products detected were ethane, hydrogen chloride and TCE; methylcyclohexane (from toluene); water, butane and traces of ethanol, 1-chloro-2-methybutane, cyclobutane, 2,2-dimethycyclobutanone and 2,3-butanediol (from THF). The conversion of organooxygen compound was very high in most of the experiments (especially in the case of ISB), producing appreciable amounts of water. Thus, these experiments also provide valuable information about the effect of water on the hydrodechlorination reaction. Experiments carried-out adding to the feed 0.5 or 5 wt.% of each organooxygen compounds are depicted in Fig. 10. Conversion of the oxygenated compounds (Fig. 11) also remained constant with time on stream. It is observed that lineal compound is more reactive than heterocyclic one, in good agreement with the behaviour reported in the literature for the hydrogenation of these compounds [33].

Unlike the rest of the heteroatomic compounds, oxygenated compounds lead to neither deactivation nor inhibition in the hydrodechlorination reaction. In the case of the highest concentration of isobutanol, its presence even enhances the performance of the hydrodechlorination reaction. Considering

Fig. 11. Evolution of oxygenated compounds conversion with time on stream (TOS). See codes in Fig. 10.

that the deactivation of Pd catalysts is mainly caused by the formation of coke deposits and the presence of HCl increases the trend of the catalysts for bearing these deposits [8,9], obtained results suggest that the presence of water modify the interaction of the HCl with the support, slightly altering the formation of active centres for coke formation.

In general, it is considered in the literature referred to hydrotreatment processes that organooxygen compounds present lower adsorption intensities than organosulphur and organonitrogen compounds, because of the lower basic character (Lewis) of the oxygen atom compared to sulphur and nitrogen atoms [34]. In the specific case of hydrodechlorination reactions, Xia et al. [16] found that oxygenated compounds (THF, ethanol, isopropanol), when used as solvents for hydrodechlorination of 2,4,4′-trichloro-2′-hydroxidiphenileter on Pd/active carbon, could act as inhibitors, especially THF. However, they carry out the reactions at lower temperatures, in liquid phase and using the oxygenated compound as solvent.

In good agreement with the reaction results, the characterization of the catalysts (BET, TEM, TG) used for the hydrodechlorination of TTCE in presence of organooxygen compounds provides results similar to those obtained for catalysts used for TTCE hydrodechlorination in absence of heteroatomic compounds.

4. Conclusions

Sulphur-, nitrogen- or oxygen-containing organic compounds studied produced very different effect on the TTCE hydrodechlorination. The nitrogenated compounds (QNL and BTA) produced fast, strong and in practice irreversible catalyst deactivation, due to the formation of solid deposits that also caused blocking of the catalytic bed. The sulphured compounds (TPN and BTT) produced strong, but partially reversible inhibition in the reaction (caused by adsorption of TPN, BTT and hydrogen sulphide), produced in the reaction. The oxygenated compounds (THF, ISB), and the water formed during heir hydrodeoxygenation, presented no appreciable effect on the reaction in the conditions tested. These results are very relevant for the practical implementation of hydrodechlorination processes, i.e. they indicate that it is very important
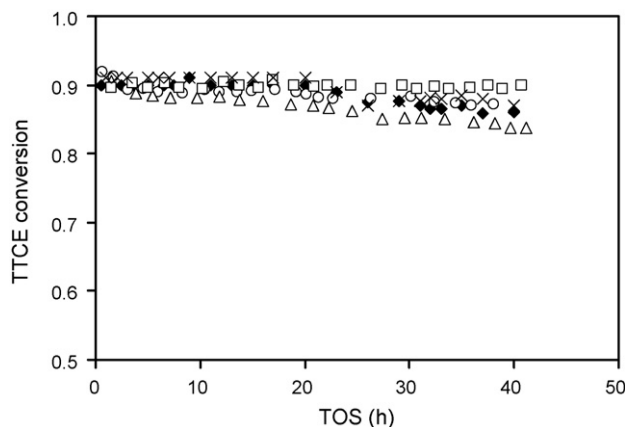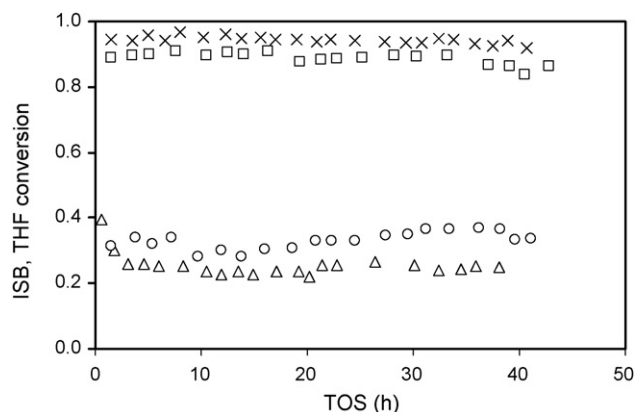

Fig. 10. Evolution of TTCE conversion with time on stream (TOS) at 250 °C, working with different concentration of oxygenated compounds: without oxygenated compounds (◆), 0.5% of THF (○), 5% of THF (△), 0.5% of ISB (×) and 5% of ISB (□).

to ensure the absence of nitrogen-containing compounds in the reaction feed.

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